

Electron states in boron nitride nanocones

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Abstract

We apply first-principles calculations to study the electronic structure of boron nitride nanocones with disclinations of different angles $\theta = n\pi/3$. Nanocones with odd values of n present antiphase boundaries that cause a reduction of the work function of the nanocones, relative to the bulk BN value, by as much as 2 eV. In contrast, nanocones with even values of n do not have such defects and present work functions that are very similar to the BN bulk value. These results should have strong consequences for the field emission properties of boron nitride nanocones and nanotubes.

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Curved nanoscale structures, of which the best known examples are carbon fullerenes and nanotubes, have been the focus of increased scientific and technological interest, due to their unique electronic and mechanical properties. [1–3]. The incorporation of pentagonal atomic rings and other topological defects into the hexagonal network of carbon nanotubes increases the local curvature and can lead to the closure of the tubes [4]. The structure of the cap depends on the specific defect included, but generally it has the aspect of a conical surface with electronic properties that are distinct from the bulk material [5]. The same applies to boron nitride (BN) nanocones, which can be formed either as the closing caps at the edges of BN nanotubes [6] or as free-standing structures [7].

An application of carbon nanotubes and nanocones is their use as cold electron sources in field emission displays [8], but current-induced structural changes [9] and oxidation [10] have been found to deteriorate the devices. BN nanotubes, on the other hand, may prove more thermally and chemically stable, as reported in a recent study [12]. Moreover, recent experiments have found that, despite being insulating, BN nanotubes yield field emission currents comparable to those of carbon nanotubes at relatively low voltages [13]. Besides the role played by geometrical field-enhancing factors, understanding the field emission properties of BN nanostructures requires a study of their electronic structure, in particular at the tip region where conical structures are present [14]. In the present study, we address the electronic structure of several such conical BN structures by first-principles calculations. As discussed in detail below, our main conclusion is that BN structures containing antiphase boundaries depict non-bulk electron states that reduce the work function, relative to the bulk BN value, by as much as 2 eV. This could strongly increase the performance of BN field emission devices relative to carbon analogues.

A conical BN structure can be geometrically constructed by a “cut and glue” process. Examples of structures built in this way and used in our calculations are shown in Fig. 1. Fig. 1(a) shows a nanocone with a four-membered ring at the apex, with a disclination angle of $2 \times 60^\circ = 120^\circ$. The high strain at the tip of the structure is energetically compensated by the absence of homopolar B-B or N-N bonds. This effect is responsible for the high

stability of BN fullerenes composed of only four- and six-membered rings [15,16]. On the other hand, rings with an odd number of atoms introduce non-BN bonds. Figure 1(b) shows a structure which has two adjacent pentagons at the apex and a single wrong bond. If a single pentagon is located at the apex, non-BN bonds are formed along the cut, generating either a B-B or an N-N antiphase-boundary. Examples of such antiphase boundaries are indicated by arrows in Figs 1(c) and 1(d). The antiphase boundaries can be of two kinds: a sequence of parallel B-B (Fig. 1d) or N-N bonds, hereafter denoted molecular B and molecular N, respectively (mol-B and mol-N, for simplicity); and a sequence of zig-zag B-B (Fig. 1d) or N-N bonds, which we shall call zig-B and zig-N, respectively. Nanocones with large disclination angles (240° and 300°) have also been observed [7]. Figure 1(e) shows one with two adjacent four-membered rings at the apex, corresponding to a 240° disclination. A saddle-like geometry associated with a -60° disclination, with 196 atoms, is shown in Fig. 1(f), with a zig-N antiphase boundary indicated by an arrow.

Each of these defects has a specific signature in the electronic structure of the material. To address this issue, we apply first principles calculations based on the Density Functional Theory [17] as implemented in the SIESTA program [18]. We make use of norm-conserving Troullier Martins pseudopotentials [19] in the Kleinman-Bylander factorized form [20], and a double- ζ basis set composed of numerical atomic orbitals of finite range. Polarization orbitals are included for both, nitrogen and boron atoms, and we use the generalized gradient approximation (GGA) [21] for the exchange-correlation potential.

The electronic structures of finite-size cones with different angles of disclination is shown in Fig. 2. The solid lines correspond to the calculated valence and conduction band edges, E_v and E_c , of the isolated BN planar sheet. The small lines indicate the position of the electron states in the region of the energy gap, relative to E_v , induced by the topological transformation of the BN sheet. No alignment between bulk and cone eigenvalues was necessary; E_v coincides with the valence band maximum of the cones within 0.1 eV, with the exception of the 300° disclination, for which there is a shift of 0.2 eV. We also performed additional calculations for a 138-atom cone with a disclination of 300° to check for cluster-size convergence.

The resulting shift in the energies of the gap levels was less than 0.06 eV.

The first four columns in Fig. 2 correspond to the four possible antiphase boundaries in a structure with a pentagonal ring at the apex (60° disclination). The general trend is that the presence of N-N bonds introduces occupied states in the lower half of the band gap, while the states associated with B-B bonds are unoccupied and in the upper half of the band gap. This is clearly seen in Fig. 2 for the zig-N, mol-B and mol-N structures. The exception to this rule is the zig-zag antiphase boundary of boron. In this case the defect states are scattered over the entire range of the gap. This exception may be partly caused by the geometry of this structure, shown in Fig. 1(c). Since a typical B-B bond length is greater than the B-N bond distance, the zig-zag antiphase boundary of boron is responsible for a large local distortion in the structure, which should affect the electronic states. Indeed, B-B bond distances of 1.7 Å and B-B-B angles as small as 70° are found in the antiphase boundary region. These values are to be compared with the B-N bond length and B-N-B angle in the graphene hexagonal network (1.45 Å and 120° , respectively). In molecular antiphase boundary nanocones, the B-B bonds are not adjacent, and as a consequence, there is enough room to accomodate them without a great distortion of the whole structure.

An important feature shown in Fig. 2 is the significant increase (by as much as 2 eV) in the energy of the highest occupied electron state for all the BN structures that contain antiphase boundaries, with the exception of the mol-B boundary. This would lead to a significant reduction of the work function of BN nanocones and cone-capped nanotubes that contain antiphase boundaries. In contrast, the structures without antiphase boundaries presented work functions very similar to that of the planar BN sheet. These results indicate that the performance of BN nanocones or cone-capped nanotubes in field emission devices would be very sensitive to the topology of the cones: those with antiphase boundaries would be much better electron emitters than the ones without these line defects.

The relationship between non-BN bonds and gap states can be further understood through the band structures of Fig. 3. In Fig. 3(a), we show the electronic structure of an infinite boron nitride plane with boron and nitrogen zig-zag antiphase boundaries pe-

riodically separated by $\sim 8.9 \text{ \AA}$. In Fig. 3(b), the same is shown for a pair of molecular antiphase boundaries. The k -direction is along the antiphase boundary. In both cases, the B-B and N-N bonds result in additional bands close to the conduction and valence band edges, respectively. The result is the closure of the gap for the zig-zag antiphase boundary and the narrowing of the gap for the molecular antiphase boundary. Note that the infinite-length antiphase boundaries lead to electron bands (due to the the crystal periodicity along the direction of the antiphase boundary) while the antiphase boundaries of the finite-size nanocones of the preceeding paragraphs lead to discrete states. The former represent the electron states far from the cone tip, while the latter include the states localized at the tip. However, in both cases the introduction of electron states associated with the antiphase boundaries, covering partially or completely the range of the electronic gap, may be associated with the surprisingly high values of field emission currents at low voltages obtained in recent experiments [13], since they may lead to a reduction of the work function at the tip.

The fifth column of Fig. 2 shows the change in the electronic structure due to the topological operation that transforms a plane into a saddle-like geometry (which has a disclination angle of -60°). The result is nearly indistinguishable from the electronic structure of the nanocone with one pentagon at the edge and the same kind (zig-N) of antiphase boundary. This result indicates that the type of chemical bonds present in the structure is more important than the specific topology in determining the existence and position of resonance and gap states, as long as the distortion is not as drastic as in the case of the zig-zag antiphase boundary of boron.

The nanocone of Fig. 1(a), with a small disclination angles and no “wrong” bonds, does not depict gap states. In contrast, the nanocone of Fig.1(e), with a large (240°) disclination angle, does have states in the gap, close to the conduction band, as indicated in the 6th column of Fig. 2. In the 7th column of the same figure we show the electronic structure of a nanocone with a disclination of 300° and a molecular antiphase boundary of nitrogen. In this case, the deviation from the planar topology is so large that several states are found

in the gap, close to the conduction and valence bands. These results indicate that extreme distortions may induce gap states in addition to the antiphase-boundary states. In that respect, we shall mention that nanocones with large disclination angles (240° and 300°) have been recently produced [7].

In summary, we have investigated the electronic structure of boron nitride nanocones. We show that cones with antiphase boundaries formed of B-B or N-N bonds introduce electron states in the energy-gap region, whereas cones without antiphase boundaries display resonant states near the band edges, related to the topological defect at the tip. Generally, states associated with the B-B and N-N bonds appear close to the conduction and valence band edges, respectively. Gap states can also be introduced by larger geometric distortions, such as those associated with large disclinations angles. Our results suggest that the changes in the electronic structure of the cones containing antiphase boundaries should strongly reduce the work function of these BN nanostructures, with important implications for understanding the field emission properties of these systems.

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FIGURE CAPTIONS:

Fig.1 - Some of the structures considered in the present study. B and N atoms are in grey and black, respectively, and hydrogen atoms saturate the dangling bonds at the edges. (a) and (b) show cones with a disclination angle $\theta = 120^\circ$. (c) and (d) show cones with $\theta = 60^\circ$. (e) is a cone with $\theta = 240^\circ$, and (f) is a saddle-like structure with $\theta = -60^\circ$. Some of the structures contain non-BN bonds: (b) has a single B-B bond at the tip, (c) has a zig-B antiphase boundary (see text), (d) has a mol-B antiphase boundary, and (f) has a zig-N antiphase boundary. The arrows in (c), (d) and (f) indicate the antiphase boundaries.

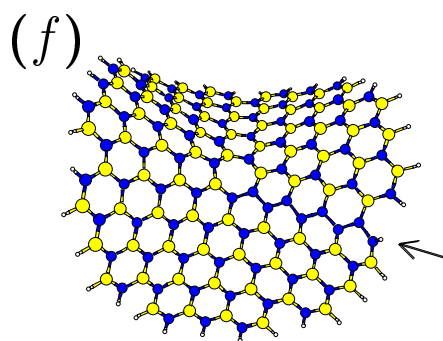
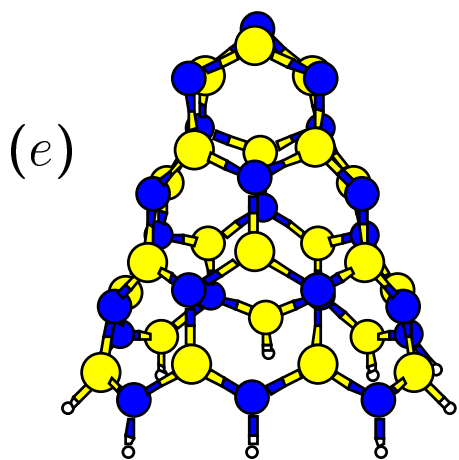
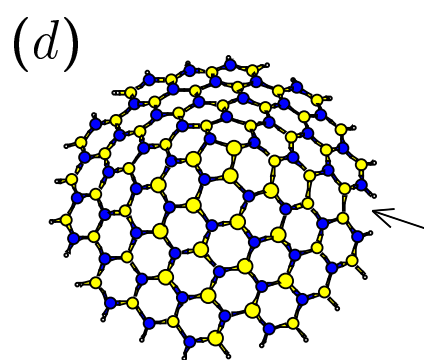
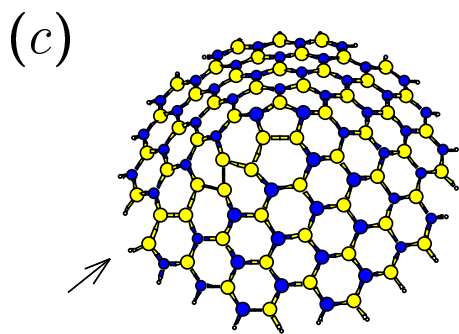
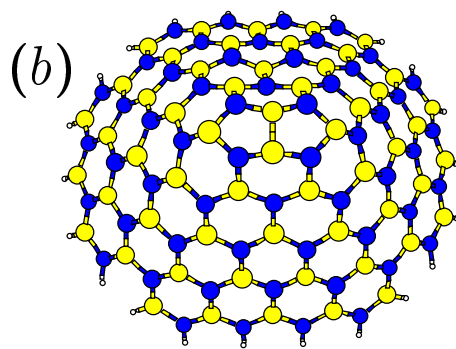
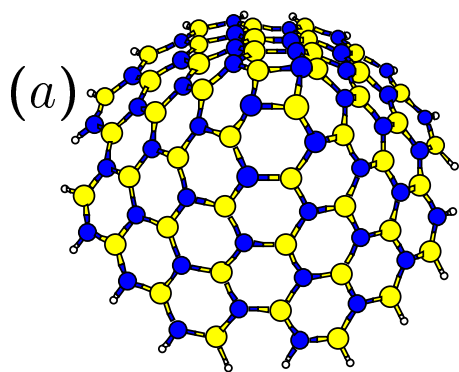
Fig. 2 - Electronic states of systems with different disclination angles θ . The first four columns correspond to structures having $\theta = 60^\circ$. The antiphase boundaries are Zig-N, Zig-B, Mol-B and Mol-N, respectively. The fifth column shows the gap states of the saddle-like structure of Fig. 1(f). The last two columns correspond to cones with large disclination angles, $\theta = 240^\circ$ and $\theta = 300^\circ$. The electronic structure of the bulk BN is used as a reference with the top of the valence band at the origin.

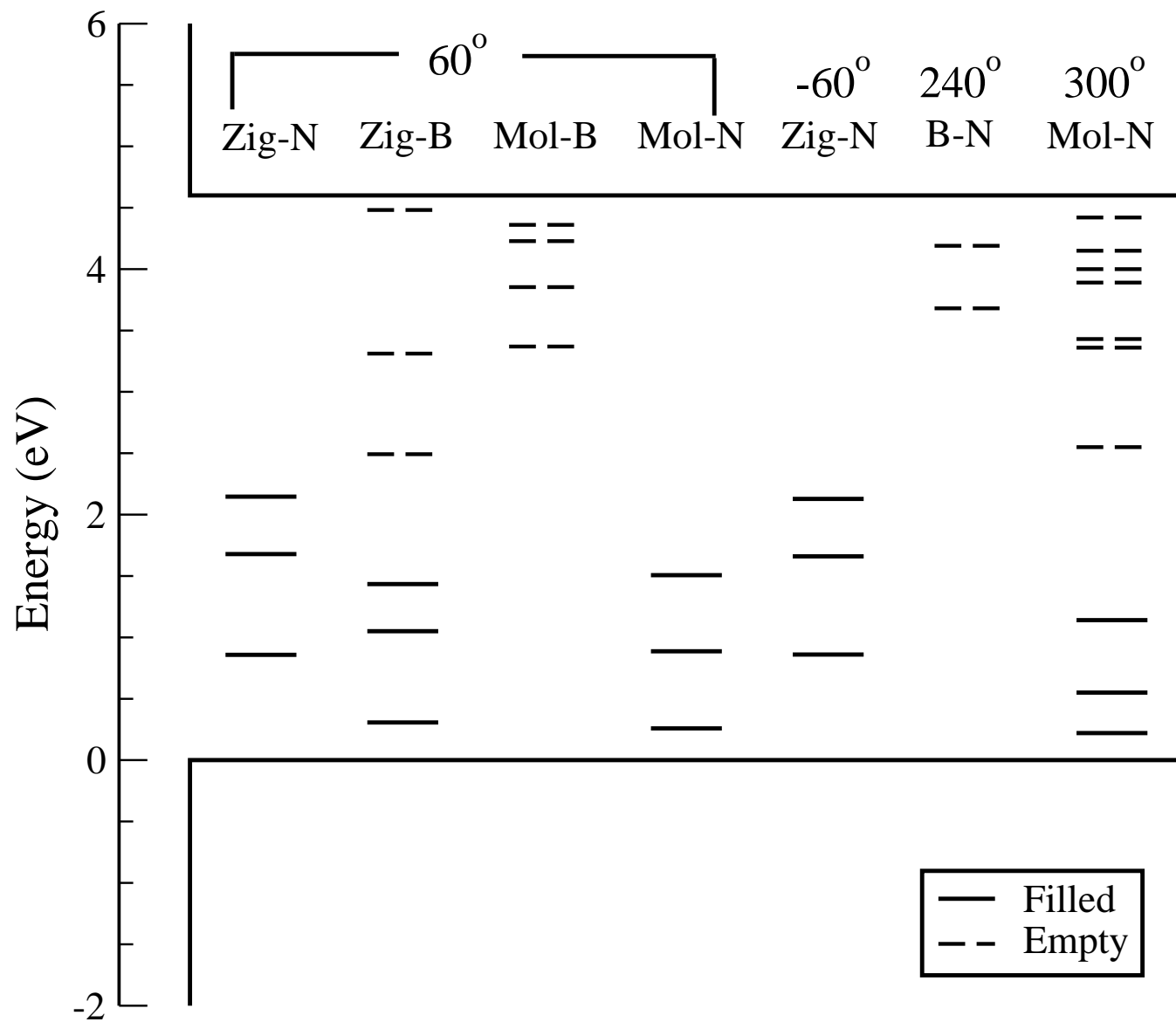
Fig. 3 - Electronic structure of infinite boron nitride planes, with antiphase boundaries periodically separated by 8.9 Å. The antiphase boundaries are zig-N and zig-B in (a) and mol-N and mol-B in (b). The k-direction is along the antiphase boundaries in both cases.

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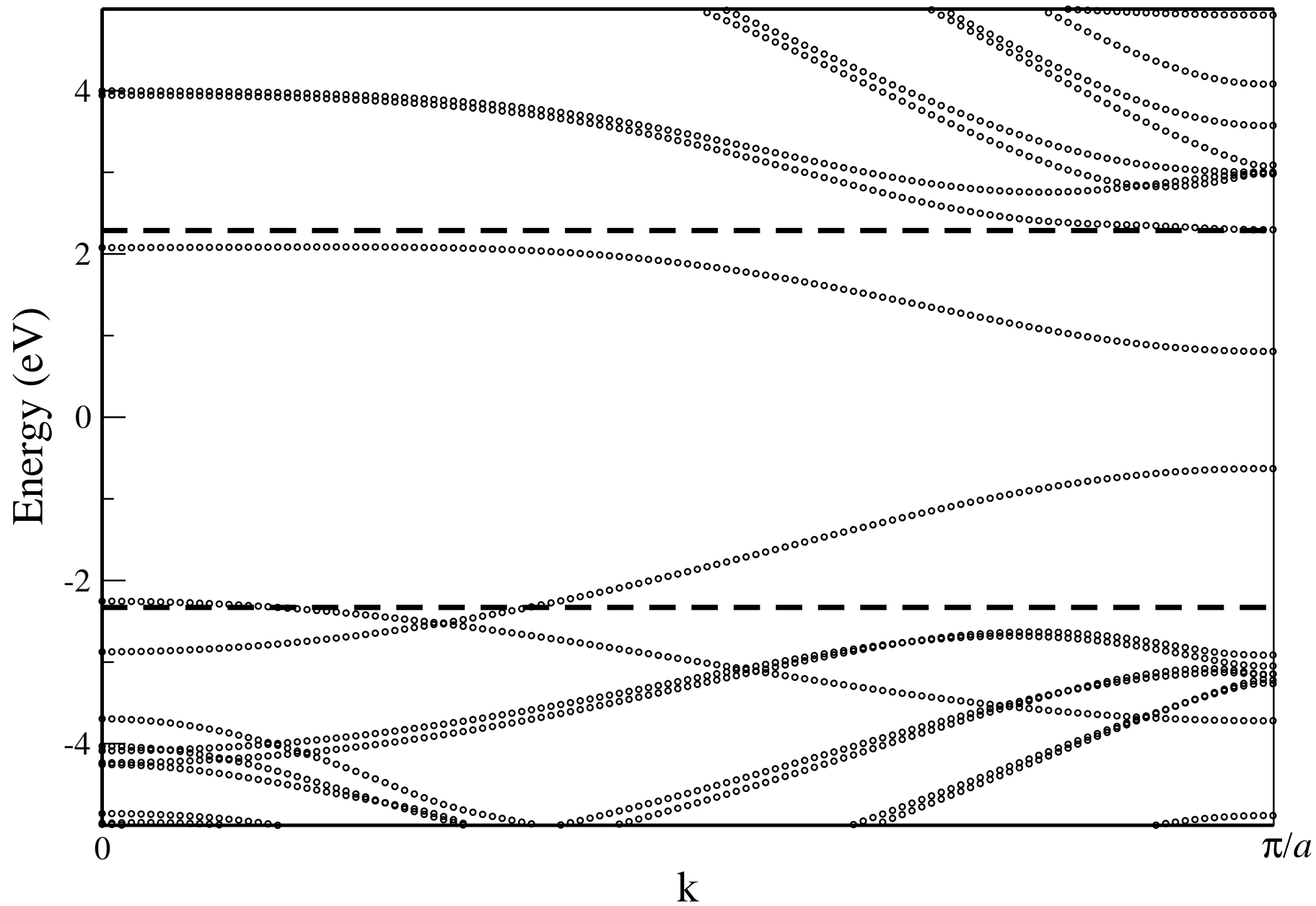
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(b)



(a)

